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(54) Title: HIGH-STRENGTH PRECIPITATION-HARDENABLE STAINLESS STEEL SUITABLE FOR CASTING IN AIR

	wt.%	
C	0.040 max.	
Mn	1.00 max.	
Si	1.00 max.	
P	0.050 max.	
S	0.015 max.	
Cr	12.00-15.50	(I)
Ni	5.75-7.25	
Mo	0.50-1.50	
Cu	1.00-4.00	
Cb	1.00-2.00	
Cb+Ta	2.00 max.	
N	0.040 max.	

(57) Abstract: A precipitation-hardenable stainless steel alloy and a cast article made therefrom are disclosed. The stainless steel alloy consists essentially of, in weight percent, about (I) and the balance is essentially iron and the usual impurities. The alloy provides a unique combination of strength, toughness, and corrosion resistance that make it particularly suitable for making cast golf club heads.

HIGH-STRENGTH PRECIPITATION-HARDENABLE STAINLESS STEEL SUITABLE FOR CASTING IN AIR

Field of the Invention

This invention relates to precipitation-hardenable stainless steels, and in particular, to a precipitation-hardenable stainless steel which is suitable for casting in air and which provides a unique combination of high strength and good toughness compared to the known grades of such steels. The invention also relates to a cast article made from a precipitation-hardenable stainless steel, in particular, a cast golf club head.

Background of the Invention

Precipitation-hardenable stainless steels have been used to make cast articles such as golf club heads. The most economical way to cast such articles is under air, rather than under a protective atmosphere such as vacuum or an inert gas. High strength, i.e., a yield strength of at least 190 ksi (1310 MPa) at room temperature, is desired for a precipitation-hardenable stainless steel for golf club heads. The known grades of high-strength, precipitation-hardenable stainless steels contain highly reactive elements such as titanium or aluminum to develop the desired strength levels during the age-hardening heat treatment. Those elements have a strong affinity for oxygen and nitrogen. Therefore, when the molten alloy is exposed to air, the alloys become "dirty" through the formation of oxides and nitrides of titanium and/or aluminum. Furthermore, the loss of the strengthening elements titanium and aluminum to oxide and/or nitride inclusions, prevents the alloy from developing maximum strength during age hardening. Also, the presence of a relatively large amount of nitrides and/or oxides impairs the castability of the alloy.

An alloy sold under the registered trademark CUSTOM 450 by Carpenter Technology Corporation has the following weight percent composition.

Carbon	0.05 max.
Manganese	1.00 max.
Silicon	1.00 max.
Phosphorus	0.030 max.
Sulfur	0.030 max.
Chromium	14.00-16.00
Nickel	5.00-7.00
Molybdenum	0.50-1.00
Copper	1.25-1.75
Columbium	8 × %C min.

The balance of the alloy is iron and the usual impurities. The CUSTOM 450 alloy is a martensitic, age-hardenable stainless steel that is typically cast and wrought, but which can be used for air casting of shapes. However, it does not provide a room temperature yield strength of at least 190 ksi (1310 MPa), even in the wrought and age-hardened condition.

In view of the foregoing, it would be desirable to have a stainless steel alloy that provides high strength and that is readily castable in air.

Summary of the Invention

The need for a high strength, castable, stainless steel alloy is essentially fulfilled by the stainless steel according to the present invention. The alloy according to this invention is an age-hardenable stainless steel alloy having the following broad, intermediate, and preferred weight percent ranges.

	Broad	Intermediate	Preferred
C	0.040 max.	0.030 max.	0.025 max.
Mn	1.00 max.	0.75 max.	0.50 max.
Si	1.00 max.	0.75 max.	0.50 max.
P	0.050 max.	0.040 max.	0.030 max.
S	0.015 max.	0.010 max.	0.005 max.
Cr	12.00-15.50	13.00-15.25	14.00-15.00
Ni	5.75-7.25	6.00-7.00	6.25-6.75
Mo	0.50-1.50	0.50-1.25	0.70-1.00
Cu	1.00-4.00	1.25-3.00	1.25-2.00
Cb	1.00-2.00	1.00-1.75	1.15-1.50
Cb+Ta	2.00 max.	1.75 max.	1.50 max.
N	0.040 max.	0.030 max.	0.025 max.

The balance of the alloy is essentially iron and the usual impurities found in commercial grades of age-hardenable stainless steels intended for similar use or service. A cast article made from this alloy provides a yield strength of at least about 190 ksi (1310 MPa) together with good toughness and ductility.

The foregoing tabulation is provided as a convenient summary and is not intended thereby to restrict the lower and upper values of the ranges of the individual elements of the alloy of this invention for use in combination with each other, or to restrict the ranges of the elements for use solely in combination with each other. Thus, one or more of the element ranges of the broad composition can be used with one or more of the other ranges for the remaining elements in the intermediate or preferred compositional ranges. In addition, a minimum or maximum for an element of the broad, intermediate, or preferred range can be used with the maximum or minimum for that element from one of the other ranges. Throughout this application, the term "percent" or the symbol "%" means percent by weight, unless otherwise indicated.

Detailed Description

A small but effective amount of silicon, up to about 1.00%, is present in this alloy for deoxidation and because it benefits the fluidity of the alloy during casting. Too much silicon leads to the formation of an undesirable amount of ferrite which adversely affects the strength provided by this alloy. Therefore, silicon is preferably restricted to not more than about 0.75%, and better yet to not more than about 0.50%.

At least about 12.00%, better yet at least about 13.00%, and preferably at least about 14.00% chromium is present in this alloy to benefit the corrosion resistance of the alloy. However, chromium is a strong ferrite forming element and therefore is limited to not more than about 15.50%, better yet to not more than about 15.25%, and preferably to not more than about 15.00% in this alloy.

Nickel is included in this alloy to provide the austenitic structure needed at the solution treating temperature, so that the alloy will transform fully or substantially fully to martensite when quenched from the solution treating temperature. Nickel also benefits the corrosion resistance and toughness of the alloy. For those reasons, the alloy contains at least about 5.75%, better yet at least about 6.00%, and preferably at least about 6.25% nickel. Too much nickel leads to an undesirable amount of retained austenite in the alloy which adversely affects the strength provided by this alloy. Therefore, nickel is limited to not more than about 7.25%, better yet to not more than about 7.00%, and preferably to not more than about 6.75% in order to avoid or substantially avoid the formation of retained austenite.

At least about 0.50% and preferably at least about 0.70% molybdenum is present in this alloy to benefit the corrosion resistance and toughness of the alloy. Molybdenum is limited to not more than about 1.50%, better yet to not more than about 1.25%, and preferably to not more than about 1.00% because, like chromium, it is a ferrite forming element. As described above, too much ferrite is detrimental to the strength provided by this alloy.

Copper contributes to the corrosion resistance of this alloy and is beneficial for the strengthening of the alloy during the aging heat treatment. Therefore, the alloy contains at least about 1.00% and preferably at least about 1.25% copper. Copper is restricted to not more than about 4.00%, better yet to not more than about 3.00%, and preferably to not more than about 2.00% because too much copper adversely affects the phase balance of this alloy by causing the formation of retained austenite. Furthermore, exceeding the solubility limit of copper in this alloy can result in the precipitation of copper at the grain boundaries, thereby adversely affecting the strength provided by the alloy.

Columbium combines with some of the nickel in this alloy to form an intermetallic strengthening phase during the age-hardening heat treatment. Accordingly, at least about 1.00% and preferably at least about 1.15% columbium is present in this alloy to benefit the high strength provided by the alloy. Tantalum may be substituted for some of the columbium on a 2 for 1 weight percent basis. Too much columbium and/or tantalum adversely affects the tensile ductility and notch tensile strength provided by this alloy. Moreover, columbium and tantalum are strong ferrite-forming elements. Therefore, the combined amount of columbium and tantalum in this alloy is limited to not more than about 2.00%, better yet to not more than about 1.75%, and preferably to not more than about 1.50%.

The balance of the alloy is essentially iron and the usual impurities found in commercial grades of age-hardenable stainless steels intended for similar use or service. Carbon, nitrogen, manganese, phosphorus, and sulfur are inevitably present in this alloy. However, the amounts of those elements are controlled because the presence of too much of them, either individually or in combination, adversely affects the strength and toughness provided by the alloy. Accordingly, carbon and nitrogen are each restricted to not more than about 0.040%, better yet to not more than about 0.030%, and preferably to not more than about 0.025% in this alloy. Manganese is limited to not more than about 1.00%, better yet to not

more than about 0.75%, and preferably to not more than about 0.50%. Phosphorus is restricted to not more than about 0.050%, better yet to not more than about 0.040%, and preferably to not more than about 0.030%. Sulfur is limited to not more than about 0.015%, better yet to not more than about 0.010%, and preferably to not more than about 0.005%.

The alloy according to this invention is preferably melted in air and cast into desired shapes, such as golf club heads. The cast alloy is then heat treated to obtain the desired level of strength. Preferably, the alloy is solution treated by heating at about 1800-2000°F (980-1095°C) for at least about one-half hour and then quenched in water. The alloy is then aged to final strength by heating at about 800-1000°F (425-540°C), preferably at about 900-950°F (482-510°C) for about 2 to 8 hours, followed by cooling in air. When thus solution treated and aged, a cast article made from this alloy provides a room temperature yield strength of at least about 190 ksi (1310 MPa), with acceptable toughness and ductility.

The terms and expressions that have been employed herein are used as terms of description and not of limitation. There is no intention in the use of such terms and expressions to exclude any equivalents of the features described or any portions thereof. It is recognized, however, that various modifications are possible within the scope of the invention claimed.

WHAT IS CLAIMED IS:

1. A precipitation-hardenable stainless steel alloy consisting essentially of, in weight percent, about:

	wt.%
C	0.040 max.
Mn	1.00 max.
Si	1.00 max.
P	0.050 max.
S	0.015 max.
Cr	12.00-15.50
Ni	5.75-7.25
Mo	0.50-1.50
Cu	1.00-4.00
Cb	1.00-2.00
Cb+Ta	2.00 max.
N	0.040 max.

and the balance is essentially iron and the usual impurities.

2. A precipitation-hardenable stainless steel alloy as set forth in Claim 1 which contains at least about 6.00% nickel.

3. A precipitation-hardenable stainless steel alloy as set forth in Claim 1 which contains at least about 13.00% chromium.

4. A precipitation-hardenable stainless steel alloy as set forth in Claim 1 which contains at least about 1.15% columbium.

5. A precipitation-hardenable stainless steel alloy as set forth in Claim 1 which contains at least about 0.70% molybdenum.

6. A precipitation-hardenable stainless steel alloy consisting essentially of, in weight percent, about:

	wt.%
C	0.030 max.
Mn	0.75 max.
Si	0.75 max.
P	0.040 max.
S	0.010 max.
Cr	13.00-15.25
Ni	6.00-7.00
Mo	0.50-1.25
Cu	1.25-3.00
Cb	1.00-1.75
Cb+Ta	1.75 max.
N	0.030 max.

and the balance is essentially iron and the usual impurities.

7. A precipitation-hardenable stainless steel alloy as set forth in Claim 6 which contains at least about 6.25% nickel.

8. A precipitation-hardenable stainless steel alloy as set forth in Claim 6 which contains at least about 14.00% chromium.

9. A precipitation-hardenable stainless steel alloy as set forth in Claim 6 which contains at least about 1.15% columbium.

10. A precipitation-hardenable stainless steel alloy as set forth in Claim 6 which contains at least about 0.70% molybdenum.

11. A precipitation-hardenable stainless steel alloy consisting essentially of, in weight percent, about:

	wt.%
C	0.025 max.
Mn	0.50 max.
Si	0.50 max.
P	0.030 max.
S	0.005 max.
Cr	14.00-15.00
Ni	6.25-6.75
Mo	0.70-1.00
Cu	1.25-2.00
Cb	1.15-1.50
Cb+Ta	1.50 max.
N	0.025 max.

and the balance is essentially iron and the usual impurities.

12. A cast stainless steel article having a yield strength of at least about 190 ksi, said article being formed from a precipitation-hardenable stainless steel consisting essentially of in weight percent, about:

	wt.%
C	0.040 max.
Mn	1.00 max.
Si	1.00 max.
P	0.050 max.
S	0.015 max.
Cr	12.00-15.50
Ni	5.75-7.25
Mo	0.50-1.50
Cu	1.00-4.00
Cb	1.00-2.00
Cb+Ta	2.00 max.
N	0.040 max.

and the balance is essentially iron and the usual impurities.

13. A cast stainless steel article as set forth in Claim 12 wherein the precipitation-hardenable stainless steel contains at least about 6.00% nickel.

14. A cast stainless steel article as set forth in Claim 12 wherein the precipitation-hardenable stainless steel contains at least about 13.00% chromium.

15 A cast stainless steel article as set forth in Claim 12 wherein the precipitation-hardenable stainless steel contains at least about 1.15% columbium.

16. A cast stainless steel article as set forth in Claim 12 wherein the precipitation-hardenable stainless steel contains at least about 0.70% molybdenum.

17. A cast stainless steel article having a yield strength of at least about 190 ksi, said article being formed of a precipitation-hardenable stainless steel alloy consisting essentially of, in weight percent, about:

	wt.%
C	0.030 max.
Mn	0.75 max.
Si	0.75 max.
P	0.040 max.
S	0.010 max.
Cr	13.00-15.25
Ni	6.00-7.00
Mo	0.50-1.25
Cu	1.25-3.00
Cb	1.00-1.75
Cb+Ta	1.75 max.
N	0.030 max.

and the balance is essentially iron and the usual impurities.

18. A cast stainless steel article as set forth in Claim 17 wherein the precipitation-hardenable stainless steel contains at least about 6.25% nickel.

19. A cast stainless steel article as set forth in Claim 17 wherein the precipitation-hardenable stainless steel contains at least about 14.00% chromium.

20. A cast stainless steel article as set forth in Claim 17 wherein the precipitation-hardenable stainless steel contains at least about 1.15% columbium.

21. A cast stainless steel article as set forth in Claim 17 wherein the precipitation-hardenable stainless steel contains at least about 0.70% molybdenum.

22. A cast stainless steel article having a yield strength of at least about 190 ksi, said article being formed of a precipitation-hardenable stainless steel alloy consisting essentially of, in weight percent, about:

	wt.%
C	0.025 max.
Mn	0.50 max.
Si	0.50 max.
P	0.030 max.
S	0.005 max.
Cr	14.00-15.00
Ni	6.25-6.75
Mo	0.70-1.00
Cu	1.25-2.00
Cb	1.15-1.50
Cb+Ta	1.50 max.
N	0.025 max.

and the balance is essentially iron and the usual impurities.

23. A cast golf club head formed from a precipitation-hardenable stainless steel consisting essentially of in weight percent, about:

	wt.%
C	0.040 max.
Mn	1.00 max.
Si	1.00 max.
P	0.050 max.
S	0.015 max.
Cr	12.00-15.50
Ni	5.75-7.25
Mo	0.50-1.50
Cu	1.00-4.00
Cb	1.00-2.00
Cb+Ta	2.00 max.
N	0.040 max.

and the balance is essentially iron and the usual impurities.

24. A cast golf club head set forth in Claim 23 wherein the precipitation-hardenable stainless steel contains at least about 6.00% nickel.

25. A cast golf club head as set forth in Claim 23 wherein the precipitation-hardenable stainless steel contains at least about 13.00% chromium.

26. A cast golf club head as set forth in Claim 23 wherein the precipitation-hardenable stainless steel contains at least about 1.15% columbium.

27. A cast golf club head as set forth in Claim 23 wherein the precipitation-hardenable stainless steel contains at least about 0.70% molybdenum.

28. A cast golf club head formed of a precipitation-hardenable stainless steel alloy consisting essentially of, in weight percent, about:

	wt.%
C	0.030 max.
Mn	0.75 max.
Si	0.75 max.
P	0.040 max.
S	0.010 max.
Cr	13.00-15.25
Ni	6.00-7.00
Mo	0.50-1.25
Cu	1.25-3.00
Cb	1.00-1.75
Cb+Ta	1.75 max.
N	0.030 max.

and the balance is essentially iron and the usual impurities.

29. A cast golf club head set forth in Claim 28 wherein the precipitation-hardenable stainless steel contains at least about 6.25% nickel.

30. A cast golf club head as set forth in Claim 28 wherein the precipitation-hardenable stainless steel contains at least about 14.00% chromium.

31. A cast golf club head as set forth in Claim 28 wherein the precipitation-hardenable stainless steel contains at least about 1.15% columbium.

32. A cast golf club head as set forth in Claim 28 wherein the precipitation-hardenable stainless steel contains at least about 0.70% molybdenum.

33. A cast golf club head formed of a precipitation-hardenable stainless steel alloy consisting essentially of, in weight percent, about:

	wt.%
C	0.025 max.
Mn	0.50 max.
Si	0.50 max.
P	0.030 max.
S	0.005 max.
Cr	14.00-15.00
Ni	6.25-6.75
Mo	0.70-1.00
Cu	1.25-2.00
Cb	1.15-1.50
Cb+Ta	1.50 max.
N	0.025 max.

and the balance is essentially iron and the usual impurities.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 00/15696

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C22C38/48 C22C38/42 C22C38/44 A63B53/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C22C A63B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 973 489 A (FIRTH-VICKERS STAINLESS STEELS LIMITED) 28 October 1964 (1964-10-28)	1-6, 8-10, 12-17, 19-21
A	claims 1-6 tables I-IV	7,11,18, 22-33
A	US 3 574 601 A (MYERS LEWIS P ET AL) 13 April 1971 (1971-04-13) claims 1-4 examples 1-3	1-33

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

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Date of the actual completion of the international search	Date of mailing of the international search report
9 March 2001	16/03/2001

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Vlassi, E

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INTERNATIONAL SEARCH REPORT

In ›nal Application No
PCT/US 00/15696

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 1997, no. 06, 30 June 1997 (1997-06-30) -& JP 09 053160 A (KAWAMURA STAINLESS KOGYO:KK), 25 February 1997 (1997-02-25) abstract	1-33
A	EP 0 496 350 A (ARMCO INC) 29 July 1992 (1992-07-29) claims 1-14 tables 1-4	1-33
A	US 4 143 258 A (MCCANN JOHN ET AL) 6 March 1979 (1979-03-06) claims 1-4	1-33

INTERNATIONAL SEARCH REPORT

Information on patent family members

In onal Application No
PCT/US 00/15696

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
GB 973489	A		NONE		
US 3574601	A	13-04-1971	CA	917964 A	02-01-1973
			DE	1957421 A	27-08-1970
			FR	2024325 A	28-08-1970
			GB	1294336 A	25-10-1972
			JP	54011245 B	14-05-1979
JP 09053160	A	25-02-1997	NONE		
EP 0496350	A	29-07-1992	US	5089067 A	18-02-1992
			AT	135057 T	15-03-1996
			AU	645147 B	06-01-1994
			AU	8788191 A	30-07-1992
			DE	69208693 D	11-04-1996
			DE	69208693 T	25-07-1996
			ES	2084195 T	01-05-1996
			JP	5043988 A	23-02-1993
			KR	214401 B	02-08-1999
			ZA	9109028 A	26-08-1992
US 4143258	A	06-03-1979	GB	1533044 A	22-11-1978
			BE	851742 A	16-06-1977
			DE	2708685 A	01-09-1977
			FR	2342120 A	23-09-1977
			IT	1073271 B	13-04-1985
			JP	52125442 A	21-10-1977
			LU	76843 A	07-07-1977
			NL	7702103 A	30-08-1977
			SE	416898 B	16-02-1981
			SE	7702094 A	28-08-1977